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Recovery of SF_6 from N_2/SF_6 Gas Mixtures by Using a Polymer Membrane

Key Words: SF_6 gas recovery, gas mixtures, polymer membrane, gas purity, recovery loss

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The purity of recovered gas, recovery loss, and gas handling speed depend on various parameters such as original gas mixing ratio, gas feeding pressure, gas flow rate, and temperature of the membrane.

The worldwide effort of reducing or even banning SF_6 gas—which has an extremely high global warming potential (GWP)—concerns not only the electric power industry but also other sectors, such as the magnesium and electronics industries. In the electric power industry, gas insulated switchgear (GIS), gas insulated lines (GIL), and gas circuit breakers (GCB) are major apparatus utilizing more or less pressurized pure SF_6. According to recent statistics [1], the cumulative SF_6 sales in the world from 1961 through 1999 amounted to 136,172 metric tons, of which power utilities accounted for 42,530 metric tons. The latter is equivalent to approximately one billion of metric tons of CO_2, if the GWP of SF_6 is taken as 23,900 [2].

One of the practical solutions of reducing or minimizing the amount of SF_6 in electric power apparatus is to utilize a pressurized gas mixture, in which a low content of an electronegative gas is mixed with an ordinary gas such as N_2, CO_2, or air. The electronegative gas may be SF_6 or one of the hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs). Among these mixtures, N_2/SF_6 is considered the most plausible alternative to pure SF_6 [3]. N_2/c-C_4F_8 or CO_2/c-C_4F_8 also has the possibility of application, since the GWP of c-C_4F_8 is as low as 8700 [2] and also c-C_4F_8 can be more easily reclaimed from mixtures by liquefaction method [4], [5].

In the case of a gas mixture that includes a low concentration of SF_6, the liquefaction method is difficult to apply [6], [7], since the boiling point of SF_6 is very low (ca. - 60 °C) compared to c-C_4F_8 (- 6 or - 8 °C). The recovery loss, or the release rate of SF_6 into the atmosphere during the liquefaction process, is estimated to be as high as 45% at a compression pressure of 5 MPa and a temperature of - 50 °C, when the concentration of SF_6 in the mixture is 10 vol.% [5]. This means that other methods more efficient than the liquefaction are necessary to recover SF_6 from a low concentration gas mixture. Such methods are also useful to enrich SF_6 as a preliminary stage before the liquefaction process.

There exist two principal recovery methods examined recently for N_2/SF_6 gas mixtures, that is, membrane separation [8]-[11] and pressure swing adsorption (PSA) [12]. The PSA method utilizes the screening action of a molecular sieve such as a zeolite, which adsorbs ordinary gases but not SF_6, which has a much larger molecular size. By using this method, more than 90% of SF_6 can be recovered from the original gas mixtures. However, it is essential to combine this method with a liquefaction process since the concentration of SF_6 in a recovered gas, or condensed gas, by the PSA method is as low as 60 vol.% for an original gas mixture with a low concentration of SF_6 [12].

This article reports an investigation of the membrane separation method. It describes experimental results on the concentration of SF_6 in a recovered gas and the recovery loss and the handling speed of a gas mixture composed of SF_6 and N_2.

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It also explains the effect of various parameters, such as gas flow rate, membrane temperature, and membrane feeding pressure. The overall characteristics show the effectiveness of the method for the recovery of SF_6 with high purity and negligibly low loss from gas mixtures with low SF_6 content.

General

The membrane separation [13] is based on the difference in the permeation rate R [Nl m^{-2} s^{-1} Pa^{-1}] that depends on the gas species and the temperature of a membrane. In a mixture composed of two gas species, the permeation rates of which are denoted R_i (i = 1, 2), the gas with the higher permeation rate penetrates the membrane faster. Thus, the selectivity α between two gases is defined as (1) and, in general, the separation is easier with the increase in α

$$\alpha = R_1/R_2 \ (> 1). \quad (1)$$

Carbon molecular sieve membrane [8], polyimide membrane [9], [10] and polycarbonate membrane [11] have been utilized for gas mixtures including SF_6. The permeation rates of some gas species, including SF_6 and N_2, for a polyimide membrane are shown in Fig. 1. The abscissa is the temperature of the membrane, which is varied by using an external heater as explained later. Among the four selected gases, SF_6 shows the lowest permeation rate. Note that the rate of SF_6 decreases with temperature, while those of the other gases increase.

The selectivity α for gas mixtures N_2/SF_6, CO_2/SF_6, and He/SF_6 is shown in Fig. 2, where R_2 in (1) corresponds to the permeation rate of SF_6. Among these mixtures, α for N_2/SF_6 is smallest, meaning that the gas separation for this composition is much more difficult than for the other mixtures. Fortunately, however, it increases from 27 at a room temperature to 100 at 100 °C.

The flow rate I_i [Nl s^{-1}] of a gas penetrating the membrane is expressed as

$$I_i = AR_i \Delta P_i \quad (2)$$

where A [m^2] is the surface area of a membrane and ΔP_i [Pa] the difference in partial pressure on both sides of the membrane for the i^{th} gas.

Experimental

The membrane we have examined is made of polyimide and has the shape of a hollow fiber of some hundreds of μm in diameter. Hundreds of such hollow fibers are bundled and installed in a shell made of stainless steel having an inlet, an exhaust, and a withdrawal tube, as shown in Fig. 3. This unit will be referred to as a membrane separator. The total area A of the membrane is 2.3 m^2 and the effective length is 0.5 m.

Figure 4 shows the experimental setup with a single separator. It consists of a membrane separator, a pressure regulator, a gas flow regulator (needle valve), gas flow meters, a tape heater, and its controller. The heater keeps the membrane temperature at 100 °C and guarantees the high selectivity, as explained in Fig. 2. When a pressurized N_2/SF_6 gas mixture is fed from the inlet into each of the hollow fibers, the gas species of larger permeation rate (N_2) penetrates the membrane radially and fills the shell. Although the gas is removed through the exhaust tube, it contains a small amount of SF_6, which results in the recovery loss. The gas remaining in the hollow fibers, rich in SF_6, is recovered through the withdrawal tube.

The gas flow rates I_c from the exhaust tube and I_b from the withdrawal tube have been measured under various experimental conditions. Under a feeding pressure P_a of the original gas mixture, I_c depends on I_b [9], with the latter being

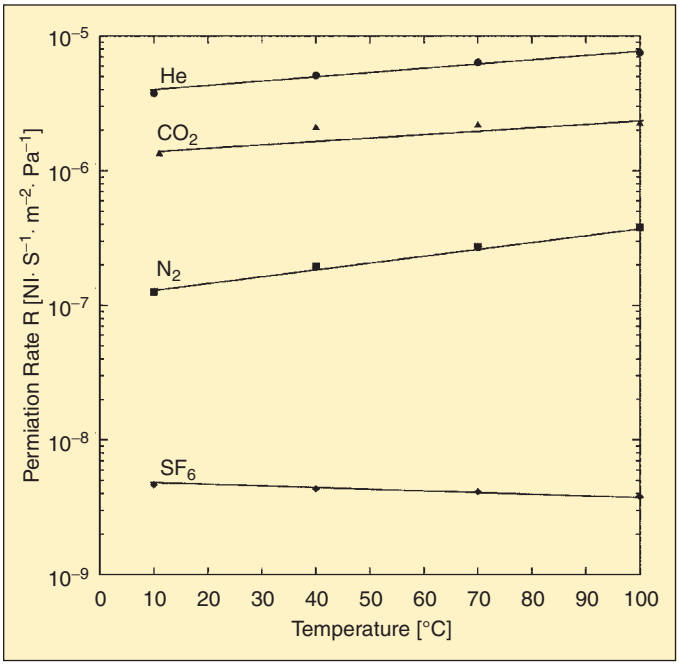

Fig. 1. Permiation rates as a function of membrane temperature.

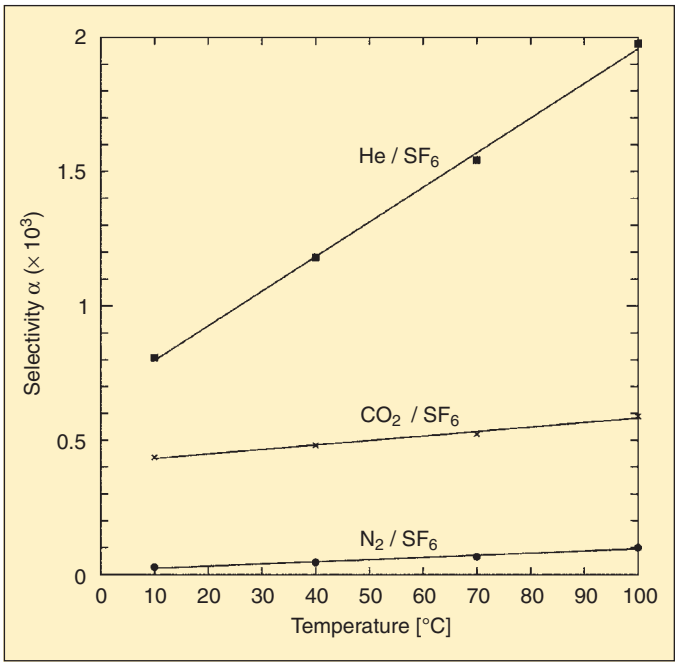

Fig. 2. Selectivity as a function of membrane temperature.

regulated using the needle valve. The concentrations of SF_6 in the withdrawn and exhausted gases, denoted as γ_b and γ_c, respectively, have been analyzed by gas chromatography. From these values the recovery loss η [%] is evaluated as

$$\eta = (I_c\gamma_c / I_a\gamma_a)\cdot 100 = I_c\gamma_c / (I_b\gamma_b + I_c\gamma_c)\cdot 100. \quad (3)$$

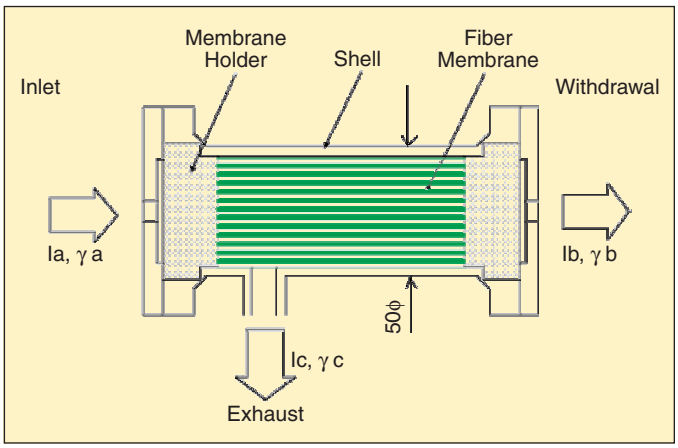

Fig.3. Membrane separator.

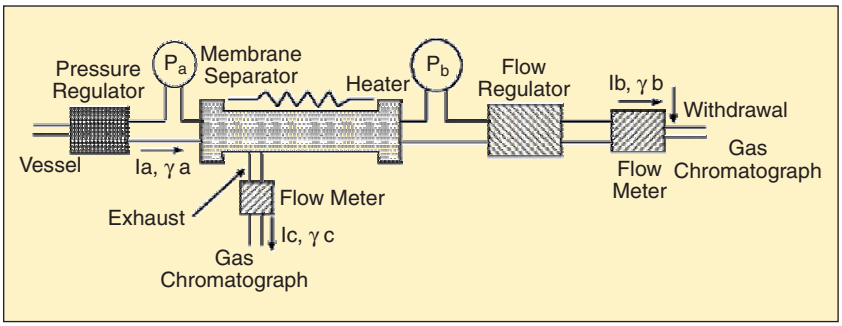

Fig. 4. Experimental apparatus with single separator.

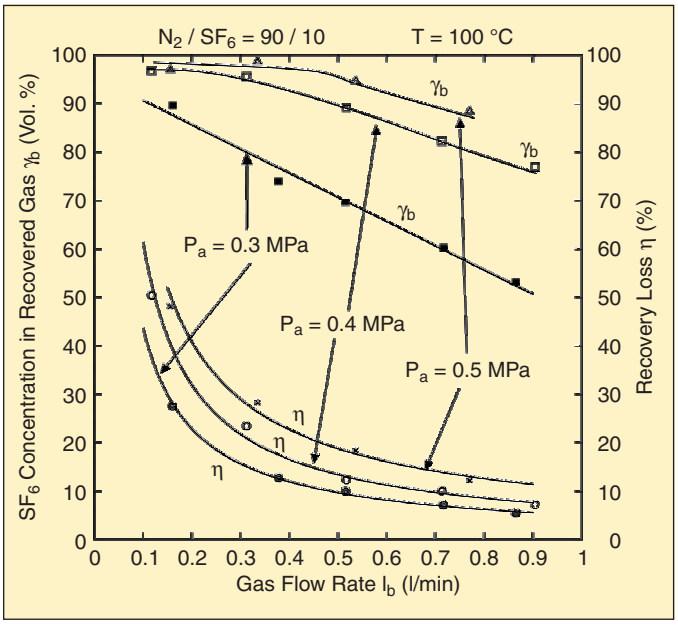

Fig. 5. SF_6 concentration in recovered gas, γ_b, and recovery loss, η.

Results

Single Separator

Figure 5 shows γ_b, the concentration of SF_6 in a recovered gas, and the recovery loss η as a function of I_b, where the mixing ratio γ_a of the original gas mixture is fixed at 10 vol.% and the feeding pressure P_a is varied as 0.3, 0.4, or 0.5 MPa. Note that γ_b and η decrease with I_b and increase with P_a.

At the condition of P_a = 0.5 MPa and I_b =0.3 Nl min^{-1}, γ_b reaches 98 vol.%, but the loss is relatively high (η > 30%). On increasing I_b up to 0.77 Nl min^{-1}, γ_b and η decrease down to 89 vol.% and 12%, respectively. The gas handling speed at this condition is approximately $I_a = I_b + I_c$ = 9 Nl min^{-1}. When γ_a is varied as 5, 10, and 20 vol.% at a fixed feeding pressure, both γ_b and η increase with γ_a as shown in Fig. 6.

These results demonstrate the good performance of the membrane separation, however, the recovery loss is large especially when the concentration of SF_6 in the recovered gas is high. In the followings, we explain a recovering method that ensures low recovery loss and also a high purity of the recovered gas.

Two Separators Connected in Cascade

Figure 7 shows the experimental system, where two membrane separators are connected in cascade. The basic concept of this connection is that the second separator recovers additional SF_6 included in the exhaust from the first separator in order to reduce the recovery loss. In the experiment, we supply the original gas mixture from a pressure tank (205 l) to the first separator S1 by using a vacuum compressor C1. Then, the exhaust gas from S1 is fed into the second separator S2, the same type as S1, through an additional compressor C2.

This system has been designed for two purposes. One is to investigate the basic characteristics of the cascade connection when a gas mixture with a constant mixing ratio is supplied into the first separator. This is referred to as the Open Cycle system. The other is to study the characteristics of this system expected when it is applied into practice, and is referred to as the closed cycle system.

Open Cycle system

During this experiment, the withdrawal gas from S2, comparatively rich in SF_6, is temporarily led into a gas container through the valve V4. As the purity of SF_6 in a recovered gas increases with an increase in pressure and the recovery loss decreases with a decrease in pressure (see Fig. 5), we have selected the pressures as $P_{a1} > P_{a2}$, where P_{a1} denotes the feeding pressure for S1 and P_{a2} for S2.

The experiment has been conducted under the condition that P_{a1} = 0.5 MPa, and P_{a2} = 0.2 MPa. The results are shown in Fig. 8, where the mixing ratio γ_a of the original gas in the tank is 10 vol.%. The figure shows the SF_6 concentrations γ_{b1} in the recovered gas from S1 and γ_{b2} from S2, the

concentration ξ of N_2 in the exhaust from S2 and the recovery loss η. The following relationship holds

$$\xi = 100 - \gamma_{c2} \quad (4)$$

where γ_{c2} is the concentration of SF_6 in the exhaust from S2. The recovery loss in the system is evaluated as

$$\eta = I_{c2}\gamma_{c2} / \left(I_{b1}\gamma_{b1} + I_{b2}\gamma_{b2} + I_{c2}\gamma_{c2}\right) \cdot 100 \quad (5)$$

where I_{b1} and I_{b2} are the flow rates of the withdrawal gases from S1 and S2, respectively, and I_{c2} is the flow rate of the exhaust from S2.

For I_{b1} = 0.43 Nl min^{-1}, for instance, the concentration of SF_6 in the recovered gas is γ_{b1} = 9 4.0 vol.%, the concentration of N_2 in the exhaust is ξ = 99.9 vol.%, and the resulting recovery loss is η = 0.49%. The gas handling speed at the condition is $I_a = I_{b1} + I_{b2} + I_{c2}$ = 7 Nl min^{-1}. Although γ_{b1} decreases with I_{b1}, ξ and η remain almost constant.

We can easily obtain a higher gas handling speed by increasing the feeding pressures or the separator size *A*. The latter will be mentioned in a later section. When the pressures have been set as P_{a1} = 0.8 MPa and P_{a2} = 0.4 MPa, and the flow rates as I_{b1} = 1.03 Nl min^{-1} and I_{b2} = 1.1 Nl min^{-1}, the handling speed I_a increases to 14 Nl min^{-1}. The purity of the recovered gas and the recovery loss are, respectively, γ_{b1} = 94.5 vol.% and η = 2.5%. The concentration of N_2 in the exhaust is ξ = 99.7 vol.%.

Closed Cycle System

In the closed cycle system, we have fed the withdrawal gas from the second separator back to the pressure tank T1. Before starting the experiment the tank has been filled with a gas mixture of SF_6 concentration γ_{a0} = 10 vol.% at 0.3 MPa. The feeding pressures are set as P_{a1} = 0.8 MPa and P_{a2} = 0.4 MPa, and the flow rates are fixed at $I_{b1} = I_{b2}$ = 1.1 Nl min^{-1}. During the experiment, we monitor the concentrations of SF_6 at various points, and also the concentration γ_a in the tank until the tank pressure decreases down to approximately 0.05 MPa.

The results are shown in Fig. 9. The concentration γ_{b1} increases from about 94 vol.% up to 98.3 vol.% in the recovered gas, while γ_{c2} decreases from 0.3 vol.% down to 0.2 vol.% in the exhaust gas. γ_a in the tank slightly increases with time, where we have stopped its monitoring after 30 min since the tank pressure decreases below the atmospheric one. The increase in γ_{b1} as well as the decrease in γ_{c2} may be attributed to the possible increase in the gas temperature due to the cyclic gas compression, which somewhat prevents cooling of the membrane. The recovery loss η during the experiment is deduced to be 2.5%, at most, from the similar result in the open cycle experiment. As the gas volume treated in 40 min amounts to 510l, the gas handling speed is 12.8 Nl min^{-1}. We need further time to recover the residual gas in the pressure tank, which depends on the evacuation ability of the vacuum compressor C1.

Discussion

Allowable Recovery Loss

As a countermeasure against the global warming trend, the Japanese electric power industry has started a voluntary action plan to reduce the emission of SF_6 gas. The plan is based on guidelines [14] prepared by the Study Committee of the Electric Technology Research Association, and chaired by one of the authors (T. T.). One of the fundamental points in the guidelines is that SF_6 gas insulated power equipment must be evacuated below P_{r1} = 15 kPa at maintenance and below P_{r2} = 5 kPa at dismantling or disposal. This provides us a relevant measure for the evaluation of the performance of reclaiming systems as follows.

Taking as an example power equipment filled with pure SF_6 at a pressure *P* = 0.5 MPa, the guidelines prescribe that

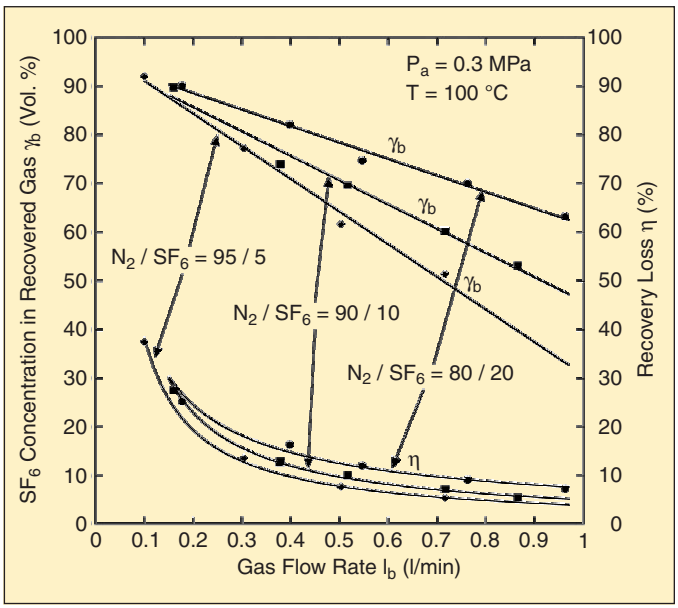

Fig. 6. SF_6 concentration, γ_b, in recovered gas and recovery loss, η, for various gas mixtures.

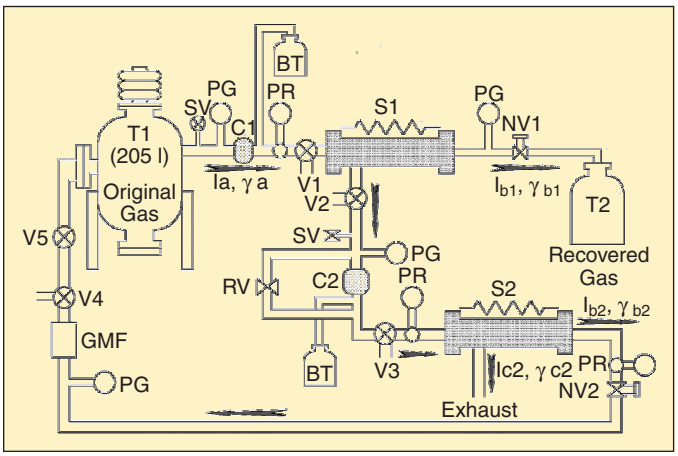

Fig. 7. Gas recovery system with two separators connected in cascade (S1, 2: membrane separators; T1: pressure tank; T2: recovery tank; BT: buffer tanks; C1, 2: compressors; PR: pressure regulators; PG: pressure gauges; NV1, 2: needle valves; V1, V4: three-way valves; V5: check valve; RV: regulation valve; SV: safety valve; GFM: gas flow meter).

the recovery loss must be smaller than $\eta_{c1} = 3\%$ at maintenance ($\eta_{c1} = (P_{r1}/P)\cdot 100$), or $\eta_{c2} = 1\%$ at dismantling ($\eta_{c2} = (P_{r2}/P)\cdot 100$). Here, we consider a gas insulation system using a N_2/SF_6 gas mixture with SF_6 concentration $\gamma_a = 10$ vol.% and gas pressure $P' = 0.75$ MPa, for instance, which would ensure the withstand voltage equivalent to that of pure SF_6 [15]. Then, the allowable losses $\eta'_{c1,2}$ for the system under the consideration can be evaluated by the following relationship assuming that the volume of the equipment is unchanged.

$$\eta'_{cj} = (P / P')\left(\eta_{cj} / \gamma_a\right)\cdot 100 \quad (j = 1,2) \tag{6}$$

where all values of η and γ are given in %.

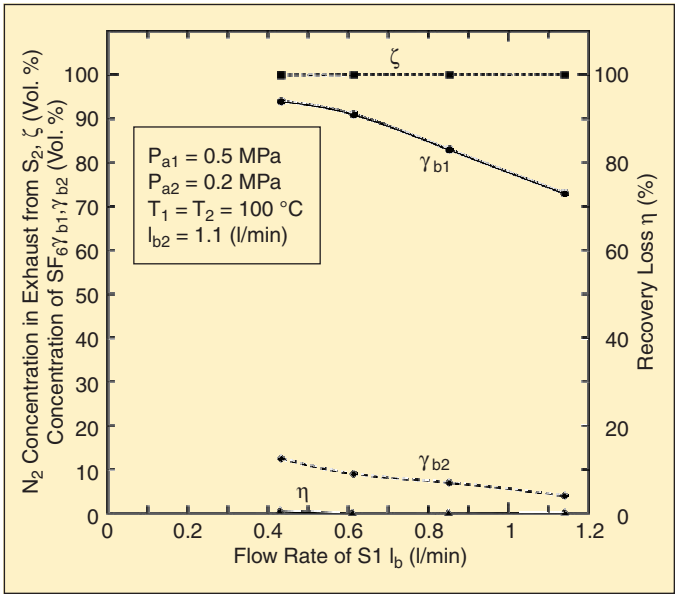

Fig. 8. Results with open cycle system.

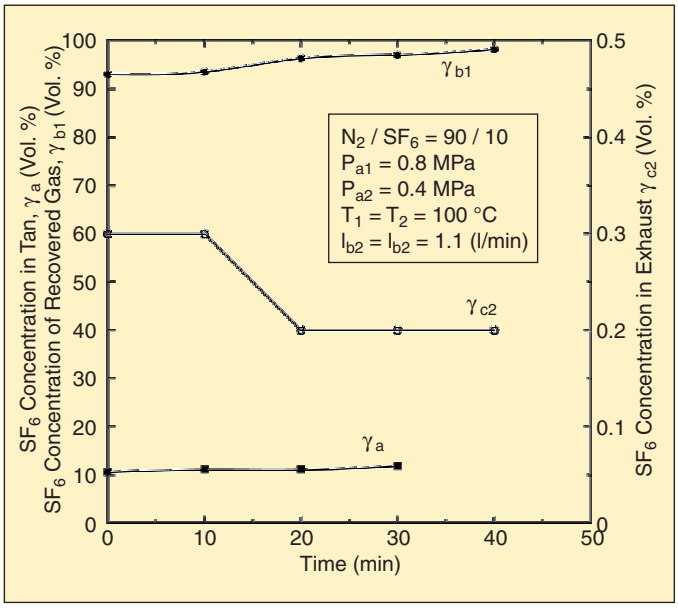

Fig. 9. Results with closed cycle system.

Thus the above prescribed losses correspond to $\eta_{c1}' = 20\%$ and $\eta_{c2}' = 6.7\%$, respectively. Whatever the reclaiming method be employed, the recovery loss for the gas mixture must be well below the above limits of allowable recovery loss, otherwise the application of a gas mixture as an alternative to pure SF_6 is not worthwhile from an environmental point of view.

It can be seen in Fig.5, where the single separator is employed, that the allowable loss requirement is satisfied under only limited experimental conditions, whereas the recovery loss with two separators in cascade easily meet the requirement.

In a strict evaluation of the recovery loss, one must take into account the amount of SF_6 in the residual gas in the power equipment after the evacuation of a gas mixture. The critical losses in this case are derived as follows

Assuming that the residual pressure in the equipment is $P_{rj}'(j = 1, 2)$, the SF_6 lost during the reclamation is $\eta(P' - P_{rj}')\gamma_a\cdot 10^{-4}$, and the SF_6 left in the equipment $P_{rj}'\gamma_a\cdot 10^{-2}$. The sum corresponds to the total SF_6 loss. Since the sum must be smaller than the residual SF_6, $P_{rj} = \eta_{cj} P\cdot 10^{-2}$, in the conventional equipment filled with pure SF_6, the following relationship holds

$$\eta \leqq \eta_{cj}' = \left(\eta_{cj} P - P_{rj}'\gamma_a\right) / \left(P' - P_{rj}'\right)\gamma_a \cdot 100. \tag{7}$$

For the same condition described above, together with $P_{rj} = P_{rj}'$, we obtain $\eta_{c1}' = 18.4\%$ and $\eta_{c2}' = 6.0\%$.

Handling Speed

In the present study with the closed cycle system, a handling speed of approximately 13 Nl min^{-1} has been obtained. The handling speed increases with the feeding pressure and the membrane size, as can be seen from (1). The handling speed of 50 Nl min^{-1}, which seems high enough for a reclaiming system in practical use, can be designed in our system by increasing the size of the membrane from $A = 2.3$ m^2 to 9 m^2. This is equivalent to doubling the shell diameter from 50 mm in the present system to 100 mm.

Reuse of the Recovered Gas

As the purity of the recovered gas is very high, the gas may be used either directly or after further purification by a liquefaction method. In a recent experiment using the open cycle system, we achieved a SF_6 concentration γ_{b1} of 99 vol.%, with a recovery loss $\eta = 0.9\%$, for a condition of $P_{a1} = 0.8$ MPa and $P_{a2} = 0.3$ MPa. This result well satisfies the critical purity given in the Japanese SF_6 recycling guide for the reuse of reclaimed gas [14], for conventional power equipment, where the purity of the reclaimed gas must be equal to or higher than 97 vol.%. It also satisfies the recycling guide published in a CIGRE report [16], where the purity equal to or higher than 98 vol.% is required.

Conclusions

The investigation of gas recovery from N_2/SF_6 gas mixtures using a polymer membrane has been reported. It has been shown that the purity of recovered gas, the recovery loss, and the gas handling speed depend on various parameters such as original gas mixing ratio, gas feeding pressure, gas flow rate, and temperature of the membrane.

A gas recovering system with two membrane separators connected in cascade has proved to be very efficient in attaining high purity in a recovered gas, with negligibly small recovery loss and high handling speed for practical use. Furthermore, this system could be applied for CO_2/SF_6, He/SF_6 and even for ternary mixtures such as $N_2/CO_2/SF_6$ without any modification in the system, where we expect much better performance in comparison with N_2/SF_6.

Osamu Yamamoto received his B.S. degree from Ritsumeikan University in 1970 and Dr. degree in electrical engineering from Kyoto University in 1982. He joined Kyoto University in 1971 as a research associate. He has been engaged in studies of high-voltage engineering especially on insulation characteristics and discharge mechanisms in gases including pressurized gas mixtures, surface flashover characteristics, and mechanisms in vacuum, and also investigations on the surge response of power transmission tower.

Tadasu Takuma received his B.S., M.S., and Ph.D. degrees in electrical engineering from Tokyo University in 1961, 1963, and 1966, respectively. He joined the Central Research Institute of Electric Power Industry in 1967, where he engaged in the study of SF_6 gas insulation, gas discharge, environmental problems of transmission lines, numerical field calculation, and new energy problems. Since 1995, he has been a professor in the Department of Electrical Engineering, Kyoto University.

He received the Maxwell Premium from the Institute of Electrical Engineers, Great Britain, in 1974, and has twice received the Book Prize for his books entitled "Numerical Calculation Methods of Electric Fields (in Japanese)" and "High Voltage—High Current Engineering" (College Textbook, in Japanese, respectively, in 1981 and 1991, from the IEE Japan.

Masayuki Kinouchi received his B.S. and M.S. degrees in 1974 and 1976, respectively, in Polymer Chemistry from Kyoto University. He joined UBE Industries, Ltd. in 1976. Since then he has been principally engaged in the research and development of polymer materials such as gas separation membranes.

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